The Atomic and Electronic Structure of Liquid N- Methylformamide as Determined from Diffraction Experiments

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Abstract

The structure of liquid N-methylformamide (NMF) has been investigated using synchrotron radiation at 77 and 95 keV. The use of high energy photons has several advantages, in this case especially the large accessible momentum transfer range, the low absorption and the direct comparability with neutron diffraction. The range of momentum transfer covered is 0.6 Å^{-1} < Q <24.0 Å^{-1}. Neutron diffraction data on the same sample in the same momentum transfer range have been published previously. In that study two differently isotope - substituted species were investigated. In order to compare neutron and photon diffraction data properly Reverse Monte Carlo (RMC-) simulations have been performed. Some modifications had to be added to the standard RMC- code introducing different constraints for inter- and intramolecular distances as these distances partly overlap in liquid NMF. RMC- simulations having only the neutron data as input were carried out in order to test the quality of the X-ray data. The photon structure factor calculated from the RMC- configurations is found to agree well with the present experimental data, while it deviates considerably from earlier X- ray work using low energy photons (17 keV). Finally we discuss whether the different interaction mechanisms of neutrons and photons can be used to directly access the electronic structure in the liquid. Evidence is presented that the elastic self scattering part of liquid NMF is changed with respect to the independent atom approximation. This modification can be accounted for by a simple charged atoms model.

1 Introduction

Liquid N-methylformamide (NMF) OHC'–NH(CH$_3$) is the simplest molecule containing the peptide bonding system O=C'–N- relevant for the structure of proteins. It has a very high dielectric constant (167.1 at 35 °C as compared to 74.8 for water). This fact has been attributed to the ability of forming hydrogen bonded chains aligning the molecular dipoles since the early measurements of Cole *et al.* 1964 [1]. The peptide system is believed to be essentially flat, having a barrier to internal rotation around the N–C' bond due to the delocalization of the O=C–N- π- bonding system [2]. The barrier to internal rotation gives rise to two different isomers: cis- and trans- NMF (trans is defined to be the isomer with

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the oxygen and the amide hydrogen on different sides of the N–C'- bond). The trans-isomer is the more stable one being present at room temperature to about 90-95% in the liquid.

These interesting properties have lead in the past to two liquid structure determinations – in spite of the relative complexity of the molecule giving rise to at least 28 independent partial structure factors, when treating the methyl protons as equivalent. First Ohtaki *et al.* [3] used conventional X-rays (Mo-K$_\alpha$: 17.4 keV) for the structure determination and interpreted their data in terms of chains of trans-NMF molecules. Next, neutron diffraction was done on two different isotope-substituted species, one being fully deuterated (NMF-d5), the other containing one hydrogen nucleus in the amide position: ODC–NH(CD$_3$) (NMF-d4) [4](this reference henceforth referred to as I). The neutron data will be used in the present paper to check the quality of the high energy photon data as well as an additional source of information for the RMC simulations.

Surprisingly, the crystal structure of NMF has been determined only recently [5], whereas there is a couple of crystal structure determinations available for similar molecules such as formamide [6, 7, 8], acetamide [7, 9, 10] and N-methylacetamide [11]. In the crystal NMF forms helical chains of hydrogen bonded trans-molecules. The molecular structure in the gas phase on the other hand has been determined by electron diffraction [12], microwave spectroscopy [13] and several quantum mechanical calculations [7, 14, 15, 16, 17]. As a result the C'=O bond is found to be substantially shorter in the gas phase then in the solid (and also shorter than in the liquid, as stated in I) indicating a higher double bond character, whereas the C'–N bond is longer.

The interpretation of X-ray diffraction experiments on liquids is typically done in the independent atom approximation neglecting the redistribution of electrons on molecule formation. This fact has been used by 'neutron diffractionists' to argue that photon diffraction has a lower inherent precision than neutron diffraction. Thinking positive one can hope to learn something about the electronic structure in the liquid by comparing neutrons and photons. However, the effect of redistribution of the valence electrons is very difficult to observe in a liquid as it is small. Its observation therefore requires a high precision on both the neutron and the photon side of the experiment. A further difficulty is the fact, that the absorption cross sections for conventional X-rays (8 to about 20 keV) in general are much larger than cross sections for neutrons, so that photon diffraction has to be done under conditions quite different from a typical neutron diffraction experiment (reflection geometry or very thin samples instead of the large samples used in neutron diffraction). As the photoelectric absorption cross section approximately decreases with E^3 this difficulty can be circumvented by using high energy photons ($\sim$ 100 keV). The conditions for performing such experiments in a reasonable time have been established recently [18]. NMF is a very promising object for observing deviations from the independent atom approximations since 75% of its electrons are valence electrons and the polarization of the bonds is expected to be high.

2   Experimental Set-up

The experiment was performed on the Hard X-ray triple axis diffractometer recently build at HASYLAB [19, 20]. The diffractometer was provisionally installed on beamline BW7 at DORIS-III, a conventional wiggler beamline not optimized for high energy use. At the time of the experiment electrons of 4.45 GeV were stored in DORIS-III. Slightly different set-ups were used for the low- and high-Q part of the spectra, one covering the range from 0.6-14.6 Å^{-1} at an incident photon energy of 76.8(8) keV, the other from 8-24 Å^{-1} at 95.5(9)

keV. The energies were determined by calibrations of a multi channel analyser with a ^{133}Ba radioactive source and from the powder lines of an (external) aluminium standard. The small scattering angles at high energies allow for a tangential move of the cooled Ge solid state detector. No provision was made to exclude the air. The beamline contains no focussing parts. The spectrometer was operated in a two- axis mode and no separation of inelastic (Compton-) scattering was attempted. The data acquisition was carried out in several scans in order to minimize errors caused by beam fluctuations and drift in general. The liquid NMF - vacuum distilled shortly before the experiment - was contained in a cylindrical glass tube of 3 mm diameter and 10 μm wall thickness. The present set-up leads to count-rates from 10000-500 s^{-1}. 100000- 400000 counts were accumulated at 670 points in about 20 h. In general, the conditions were quite similar to the previously described experiment on glassy SiO$_2$ [18].

3   Data correction and error estimation

The raw data - after summing up the individual scans - are shown in figure 1. These data were subsequently corrected for background (mainly scattering from air and sample container), absorption, multiple scattering, polarization of the incoming beam, the variation of the solid angle seen by the detector as a result of the changing sample to detector distance (tangential movement, see above) and the increased detection efficiency for inelastically scattered photons. μr is 0.027 at 76.8 keV (with μ being the total absorption coefficient and r the radius of the sample) and hence both absorption and multiple scattering corrections are very small. Air scattering is the dominant background contribution, especially at low Q's. The main error sources in this study are therefore believed to be the instabilities induced by a different response of the main detector and the monitoring system to the synchrotron beam fluctuations, the knowledge of the degree of linear polarization of the monochromatic beam (assumed to be known within 1%), the distance sample to detector (equally known approx. within 1%) and the energy calibration. The mean energy shift of the inelastically scattered photons at Q=23 Å^{-1} is 1.6 keV at 95.5 keV. The effect of an increasing detection efficiency for those photons is estimated to be a 1% effect. For a more detailed description of the data correction procedure the reader is referred to [18]. The fully corrected and normalized intensity is presented in figure 2.

4   Simulation details

In RMC- simulations [21] a suitable number of atomic or molecular entities is placed in a cubic (or differently shaped) simulation box. A Markov- chain is generated accepting moves provided the move is improving the agreement with experiment, or if a random number in the range [0 : 1] is less than $\sum_i^{N_{exp}} \exp(-\Delta\chi_i^2/2\sigma_i^2)$ where the sum extends over all N_{exp} independent experiments. Otherwise the move is rejected. $\Delta\chi^2$ is the difference between the χ^2 of the old and the new configuration, where χ_i^2 is defined here as:

$$\chi_i^2 = \sum^{N_{\text{points}}} [S(Q)_{conf,i} - S(Q)_{exp,i}]^2 \tag{1}$$

where the sum extends over all N_{points} points in Q-space , S(Q) is defined by Eqs. 2 and 4, σ_i^2 is a measure of the assumed error in data set i, the subscript $conf$ refers to the $S(Q)$ calculated from the configuration generated and the subscript exp to the experiment. RMC simulations in polyatomic molecular systems are not as straightforward as in atomic

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systems. It is accepted, that the molecules should not be treated as rigid because the molecular part of the scattered intensity is then reproduced poorly. If on the other hand the atoms are treated as free one has to introduce the information that the atoms are connected and form a molecule. The approach used by Radnai *et al.* [22] based entirely on coordination constraints was found to be unsuitable in our case, since in NMF inter- and intramolecular distances overlap. As a consequence two problems arise: a_1 and a_2 are the distances between which a next neighbour of type B is expected around an atom of type A *within* the molecule (so that $a_1 \leq r_{AB}(\text{intramolecular}) \leq a_2$) and a_3 is the smallest distance at which a molecule of type B on a *different* molecule is expected around A. In the standard RMC code no distinction is made between inter- and intramolecular distances, thus even if $a_1 \leq a_2 \leq a_3$ error messages occur as the intramolecular distances between a_1 and a_2 violate the constraint that no AB distance should be present below a_3 (hard core radius). This is still not disadvantageous, but if $a_1 \leq a_3 \leq a_2$ the RMC code tries to satisfy both the coordination constraint between a_1 and a_2 and the hard core radius a_3. As a result all intramolecular distances are now comprised between a_3 and a_2 what is not intended. If finally $a_3 \leq a_1 \leq a_2$ there are real *inter*molecular distances between a_1 and a_2 and hence the total coordination in the range $[a_1 : a_2]$ is no longer known. The only way to treat this problem is to fix explicitly which atoms belong to the same molecule and to give different coordination constraints and cut-off radii for inter- and intramolecular distances. This can not be done with the standard RMC, version III code[23].

In the present simulation a 9 site model with 216 molecules corresponding to 1744 atoms was used. The distance of closest approach was fixed to 2.0 Å for all intermolecular distances except the O$\cdots$H–N were it was 1.5 Å. The molecular density was taken to be 0.01022 Å^{-3} corresponding to a half box length of 13.85 Å. The intramolecular constraints are given in Table 1 and are chosen to give essentially planar trans-molecules, where the methyl protons are free to rotate around the N-C bond. The range in which the intramolecular distances can fluctuate is chosen to be four times the Debye-Waller factor as given by Kitano *et al.* [12].

5 Analysis

In order to assess the quality of the high energy photon data a RMC simulation (modified as described above) has been carried out using only the neutron data from I as input. From the configurations generated we calculated the corresponding photon scattering. We compare the result to our experimental data as well as to the data of Ohtaki *et al.* [3] obtained with Mo-K$_\alpha$ X-rays.

The RMC fit to the two neutron data sets and its first order difference is shown in figure 3 in Q-space. The definitions of the functions shown are:

$$
\begin{aligned}
S(Q) &= \frac{\left(\dfrac{d\sigma}{d\Omega}\right)_{dist}}{(\sum_{N_M} b_i)^2} \\
g_n(r) &= 1 + \frac{1}{2\pi^2 \rho r} \int_0^{Q_{max}} Q S(Q) \sin(Qr) dQ,
\end{aligned}
\tag{2}
$$

where $(d\sigma/d\Omega)_{dist}$ is the distinct differential cross section, the sum is extended to all N_M atoms in the molecule, b_i is the neutron scattering length of atom i, ρ is the macroscopic number density, Q_{max} is the largest accessible momentum transfer where $S(Q) = 0$, $S(Q)$ is the neutron weighted structure factor and $g_n(r)$ is the neutron weighted pair distribution

function. The agreement between simulation and experiment is good within the statistics given by the number of sites and the chosen σ- parameter for the total structure factors, but not perfect for the hydrogen first order difference in the low-Q region. The first order difference is given here by:

$$S_{N-H} = S_{d5} - \frac{(\sum_{N_M(d4)} b_i)^2}{(\sum_{N_M(d5)} b_i)^2} S_{d4} \tag{3}$$

Note, however, that the first order difference has been enlarged by a factor of 5. The fit is considered to be good enough for our purposes ($\sqrt{\chi^2/N_{\text{points}}}$ defined by Eq. 1 is 0.0032 for NMF-d5 and 0.0043 for NMF-d4).

The next question to ask is whether or not the configurations consistent with the neutron data are also consistent with the photon diffraction data. With definitions analogous to those appearing in Eq. 2:

$$\begin{aligned} i(Q) &= \frac{\left(\frac{d\sigma}{d\Omega}\right)_{dist}}{(\sum_{N_M} f_i)^2} \tag{4} \\ g_x(r) &= 1 + \frac{1}{2\pi^2 \rho r} \int_0^{Q_{max}} Q i(Q) \sin(Qr) dQ \end{aligned}$$

the comparison RMC(neutrons) *versus* experiment(photons) is done in Fig. 4 and 5. $i(Q)$ is here the photon weighted structure factor, $g_x(r)$ the photon weighted pair distribution function and f_i the form factor of the ith atom.

Focussing first on the real space comparison two things should be noted: First, $g_x(r)$ is not equal to zero at $r \leq r_{cut}$ for the Fourier- transform of the RMC $S(Q)$ - where r_{cut} is the smallest internuclear distance. This is known to be caused by the fact that the terms $f_i f_j/(\sum f)^2$ are not constant in Q. Second, there is a much larger deviation from zero for the Fourier-transform of the experimental $S(Q)$. It is current practice to back Fourier-transform the deviation of $g_x(r)$ from zero at low r to get an idea about the size and the location of systematic errors in Q-space [24] However, this approach is known to be incorrect, as $g_x(r)$ may deviate from zero even for data completely free from systematic errors. We have therefore chosen to use the following 'correction'-function instead:

$$K(Q) = (\sum f)^2 \frac{4\pi\rho}{Q} \int_0^{r_{cut}} [g_x(exp) - g_x(\text{RMC})] \sin(Qr) dQ \tag{5}$$

$K(Q)$ will be shown to be largely related to deviations from the independent atom approximation.

The form factor of a spherically symmetric atom is given by [25]:

$$f_{iaa}(Q) = \sum_{i=1}^{Z} 4\pi/Q \int_0^\infty \psi_i^2(r) r \sin(Qr) dr \tag{6}$$

where f_{IAA} is the form- factor of the unperturbed atom, Z is the number of electrons within that atom and ψ_i is the wave-function of the ith electron. Using Roothaan-Hartree-Fock (RHF) atomic wave-functions as tabulated by Clementi *et al.* [26] the above integral can be solved analytically.

Now leaving the independent atom approximation, a very simple approximation of atoms in molecules is the assumption that the electron cloud of the atoms keep its form and spherical symmetry but that the atoms can adopt net charges [27]. As a consequence the

valence shell of the respective atom is contracted or expanded, while the core electrons remain unaffected:

$$\psi'^2_{valence}(r) = \psi^2_{valence}(\kappa r) \tag{7}$$

The simplicity of this approach keeps the integrals of Eq. 6 to be solved analytically. The calculations are presented in the appendix. A comparison between $(\sum f_i)^2_{iaa} - (\sum f_i)^2_{cm}$ and $K(Q)$ is done in Fig. 6 (iaa for independent atom approximation and cm for charged atoms model). The charges of the atoms have been taken from formamide in the solid state [8] and it is assumed that the methyl group takes the charge of one amide hydrogen. The charge parameters are given in Table 2. Using now the modified form-factors $f_{i,cm}$ in the analysis the low r deviations of $g_x(r)$ are very much reduced as shown in Fig. 5, except for the peak at 0.3 Å. Given the crude model used, this result is very satisfying. One can ask now whether the peak at 0.3 Å also has a physical meaning or is caused by experimental errors, but further analysis seems to be speculative without supporting quantum-mechanical calculations.

In Fig. 7 $i(Q)$ from our experiment and the one from Ohtaki's experiment [3] are compared to the RMC result (with the neutron measurements as input only). The discrepancies of Ohtaki's data in the first diffraction peak are immediately evident. This is rather astonishing as in the region $Q > 3\text{Å}^{-1}$ - dominated by intramolecular distances - the agreement between Ohtaki's data and the simulation is very good, even better than the agreement achieved in the present study. It is noted that Ohtaki's data do not extrapolate to the correct low Q limit given by the compressibility. On the other hand the agreement between the high energy photon result and the shape of the first maximum predicted by the neutron result is nearly perfect. Concluding, there seems to be a larger problem in Ohtaki's data analysis and the conclusions drawn in his paper should therefore be accepted with care.

Including the hard X-ray data in the RMC simulations, does not remove the slight discrepancies between simulation and experiment in the range from 3-8 Å^{-1} still present in Fig. 7. From another point of view - these discrepancies are not of a type which could be removed by simply moving atoms in the box within the given constraints. Hence, as stated above, these discrepancies are caused either by systematic errors still present or by deviations form the independent atom approximation not accounted for by the primitive model used. This fact also highlights, that the x-ray diffraction pattern is *predicted* by the neutron diffraction data, and the x-ray data are in excellent agreement with the neutron data.

Likewise, introduction of 10% cis- molecules does not substantially improve the fit. Nevertheless, the configurations generated in this way might be closer to reality, as it is known that a certain percentage of cis-molecules are present in the liquid. The cis/trans isomerism only changes rather long intramolecular distances - smeared by large amplitude vibrational motions - which can be modelled by intermolecular distances without coming into conflict with the imposed constraints.

Finally, one aim of the present study was to test the conclusion drawn in I, that the molecular structure of liquid NMF is more like in the solid and not like the gas phase structure, hence, answering the question, whether long range order is a necessary condition for the found increased delocalization of the π-electron bonding system. The r-space resolution should be sufficient to resolve the C'–N and the C'=O distances if the gas- phase model of the molecule is valid and at high Q the respective interference pattern should be observed. Different from the neutron case these distances are not significantly obscured by hydrogen-heavy atom distances. This is illustrated in Fig. 8, but it is also apparent from the figure

that the counting statistics reached at high Q-values so far is not sufficient to support the finding from I. The beam fluctuations mentioned in chapter 3 also contribute to the uncertainty in S(Q). In this respect, the data quality will probably improve in the near future, especially with the introduction of an area detector. It is also noted, that the Q-range up to about 14 Å^{-1} covered by conventional X-rays is not very conclusive for answering the question posed.

6   Conclusion

The structure of liquid NMF has been investigated using the recently reported methods for high energy photon diffraction. The structure factor derived is shown to be in much better agreement with the information available from neutron diffraction measurements than the earlier study of Ohtaki *et al.* using low energy photons (conventional Mo-K$_\alpha$-radiation). In the intermediate Q-range from about 3-8 Å^{-1} some discrepancies between the experimental self- scattering intensity and the self-scattering predicted by the independent atom approximation are observed. These discrepancies are accounted for by a simple charged atoms model, based on charge parameters from solid state formamide. The introduction of charged atoms largely improves the low-r behavior of $g_x(r)$. Although promising for testing a finding from neutron diffraction - that the intramolecular structure of liquid NMF is closer to the solid state structure than to the structure of the gas phase - this aim could not be reached as the counting statistics were not good enough at high Q values.

High energy photon diffraction is likely to see considerable progress and will be a useful tool for understanding the physics of systems without long-range order. Its most outstanding property will be the ease with which information from neutron and photon diffraction can be combined.

7   Appendix

In this appendix the solution of the integrals appearing in Eq. 6 will be sketched, first in the independent atom approximation using RHF wave-functions, then in the charged atoms model given by Eq. 7. RHF wave-functions are of the form:

$$\psi_i = \sum_p C_p \chi_p \tag{8}$$

where C_p are the expansion coefficients of the basis functions χ which are of the Slater type:

$$\chi_{p\lambda\alpha}(r,\theta,\phi) = R_{p\lambda\alpha}(r)Y_{\lambda\alpha}(\theta,\phi) \tag{9}$$

with

$$R_p(r) = \text{const.}(\xi_p) \ r^{n-1}e^{-\xi_p r} \tag{10}$$

where n is the quantum number of the basis function, λ indicates the symmetry species, α the subspecies of the electron wave-function and $\xi_{p\lambda\alpha}$ the orbital exponent (The angular dependence of the 2p-type orbitals averages out). Inserting the RHF wave-functions into Eq. 6 creates integrals of the type:

$$\frac{1}{Q}\text{const.} \int_0^\infty r^{n_1+n_2-1}e^{-(\xi_1+\xi_2)r} \sin(Qr)dr \tag{11}$$

which can be solved analytically [28]. With e. g. $n_1 = 1$ and $n_2 = 2$ the above integral equals to:

$$\frac{8}{\sqrt{3}} \frac{C_1 C_2}{Q} \xi_1^{1.5} \xi_2^{2.5} [(\xi_1 + \xi_2)^2 + Q^2]^{-1.5} \sin(3 \arctan[Q/(\xi_1 + \xi_2)]) \tag{12}$$

When modifying the wave-functions as in Eq. 7 the term in Eq. 12 e. g. has to be modified to:

$$\frac{8}{\sqrt{3}} \frac{C_1 C_2}{Q} \xi_1^{1.5} \xi_2^{2.5} [(\xi_1 + \xi_2)^2 + \left(\frac{Q}{\kappa}\right)^2]^{-1.5} \sin(3 \arctan[\frac{Q}{\kappa}/(\xi_1 + \xi_2)])/\kappa^2 \tag{13}$$

It should be noted that the $Q \to 0$ limit of $\sum f^2$ in the charged atoms model is no longer $\sum Z_i^2$ but $\sum (Z_i + q_i)^2$, where Z_i is the nuclear charge and q_i are the partial charges of the atoms. q_i is related to κ by:

$$q_i = Z - [N_{\text{valence}}/\kappa^3 + N_{\text{core}}] \tag{14}$$

where N_{valence} is the number of valence electrons in the independent atom and N_{core} is the number of core electrons.

8   Acknowlegement

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Figure 1: The high energy X-ray raw data
From top to bottom: scattering from NMF in a glass tube, from the empty glass tube, and background scattering (mainly air scattering). The high-Q data are divided by 10 for better visibility. The ratio counts/monitor counts is larger for the high-Q scans as the distance sample/detector is shorter and hence the sampled solid angle larger.

Figure 2: The fully corrected and normalized data
Full line: isotropic part of the scattering intensity (Self scattering + Compton part); broken line: experimental intensity. Note that the slightly higher level of the isotropic part in the high-Q region is caused by the higher energy (lower relativistic correction) of the photons used. Insert: Zoom into the region Q > 6 Å^{-1}.

Figure 3: RMC- fit to the neutron data
From top to bottom: Fit to the NMF-d5 data, fit to the NMF-d4 data, the resulting hydrogen first order difference. Full line: RMC simulation, broken line: experimental data from I. The first order difference is enhanced by a factor of 5.

Figure 4: Comparison RMC(neutron data) *versus* experiment (high energy photons)
Full line: high energy photons, self scattering in the independent atom approximation, broken line: high energy photons, self scattering from the charged atoms model (see text), points: RMC simulation, neutron data as input only.

Figure 5: Comparison RMC(neutron data) *versus* experiment (high energy photons)
Same as Fig. 4, but in real space.

Figure 6: Comparison $K(Q)$ *versus* $[(\sum f_{iaa})^2 - \sum (f_{cm})^2]$
Full line: $K(Q)$ is a 'correction'- function defined in the text, broken line: difference between the self-scattering calculated from the independent atom approximation and the charged atoms model.

Figure 7: Comparison of low energy photons with high energy photons and neutrons
Full line (with diamonds): low energy photons (from Ohtaki *et al.* [3], broken line (longer lines): RMC simulations, neutron data as input only, broken line (shorter lines): high energy photons (this work), self scattering in the charged atoms approximation, dots: high energy photons (this work), self scattering in the independent atom approximation.

Figure 8: Comparison gas-phase model *versus* solid state model of the intramolecular structure
Diamonds: experimental points, solid line: intramolecular i(Q) based on the gas phase model with C'O = 1.22 Å and C'N = 1.35 Å, broken line: intramolecular i(Q) based on the solid state model with C'O = 1.26 Å and C'N = 1.29 Å, points: smoothed experimental points.

Table 1: Constraints used for the RMC simulations

	N		N-$\underline{H}$		C'		C		O		C'-$\underline{H}$		C-$\underline{H}$	
N-$\underline{H}$	0.86	1.15	—		1.78	2.16	1.92	2.33	2.97	3.33	1.86	2.48	—	
C'	1.21	1.38	1.78	2.16	—		2.29	2.58	1.19	1.35	0.94	1.26	—	
C	1.36	1.56	1.92	2.33	2.29	2.58	—		2.64	3.09	3.10	3.51	0.91	1.23
O	2.17	2.38	2.97	3.33	1.19	1.35	2.64	3.09	—		1.89	2.25	—	
C'-$\underline{H}$	1.79	2.18	1.86	2.48	0.94	1.26	3.10	3.51	1.89	2.25	—		—	
C-$\underline{H}$	1.89	2.30	—		—		0.91	1.23	—		—		1.48	2.00

All distances in Å. Left number lower limit, right number upper limit for the respective intramolecular distance.

Table 2: Charge parameters for the charged atoms model (cm)

	N	N-$\underline{H}$	C'	C	O	C'-$\underline{H}$	C-$\underline{H}$
κ	0.9567	1.1856	1.0465	1.0093	0.9712	1.0102	1.0357
q_i	−0.78	+0.40	+0.51	+0.10	−0.55	+0.03	+0.10